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CHEMICAL SHIFTS AND SOLID–ECHO IN HOMONUCLEAR SPIN SYSTEMS

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Introduction

The Van-Vleck second moment M_2 provides detailed information about both the geometrical arrangement and thermal motions of the nuclei in solids. So the accurate measurement of M_2 is important problem in solid state NMR. At the present time the solid-echo ($90^0{}_Y-\tau-90^0{}_X-t$) is the main pulse method for M_2 measurement [1,2]. In solid with only one nuclear species (homonuclear spin system) the formation of the solid-echo signal is due to the interactions between nuclear magnetic dipole moments. The dipole-dipole interactions give also the main contribution to M_2. However, in solids there are always the nuclear-electron interactions (chemical shift interactions). These interactions also give the contribution to M_2 and one may not be such small for instance for ^{19}F nuclei.

The main purpose of this work is the analysis the influence of the nuclear-electron interations on the echo signals in homonuclear spin systems.

Results and discussion

The general expression for the solid-echo signal obtained in [3] at the delta approximation of the RF pulse has the form

$$V(t,\tau) = G_0(t)G_0(\tau) - (a_{11}/M_2^2)\, dG_0(t)/dt\, dG_0(\tau)/d\tau + \dots \quad . \qquad (1)$$

Here M_2 is the second moment,

$$a_{11} = Tr\{[I_X, H_{int}]\,[H, I_X]\}/Tr(I_X^2)\ , \qquad (2)$$

and

$$H = \exp(-\,i\pi\, I_X/2)\, H_{int} \exp(i\pi\, I_X/2)\ . \qquad (3)$$

In Eq.(3) H_{int} is the interaction Hamiltonian of the nuclear spin system in co-ordinate frame rotating with Larmor angular frequency $\omega_0=\gamma B_0$ about Z axis ($\mathbf{B}_0 \| Z$).

The function $G_0(t)$ in Eq.(3) describes the shape of the free induction decay (FID) – the signal NMR which is observed after the 90^0_Y -pulse and which is proportional to $Tr\{I_X(t)\, I_X\}$.

For the homonuclear spin system the interaction Hamiltonian H_{int} is

$$H_{int} = H_D + H_{CS} \ , \qquad (4)$$

where H_D is the secular dipolar Hamiltonian

$$H_D = \Sigma_{(i<j)} D_{ij} (2I_{iZ}I_{jZ} - I_{iX}I_{jX} - I_{iY}I_{jY}) \ , \qquad (5)$$

$$D_{ij} = (1/4\pi)\, \gamma^2 h\, (1 - 3\cos^2\theta_{ij})\, R_{ij}^{-3} \qquad (6)$$

and H_{CS} is the secular chemical shielding Hamiltonian

$$H_{CS} = \Sigma_{(i)}\, \sigma^i_{ZZ}\, I_{iZ} \ . \qquad (7)$$

In the above expressions R_{ij} and θ_{ij} are polar co-ordinates for a pair of spins to the Z axis and σ^i_{ZZ} is ZZ-component of the chemical shielding tensor of nucleus i.

Using Eqs.(4)÷(7) we obtain from Eq.(2)

$$a_{11} = -\, M_{2D} \ , \qquad (8)$$

where M_{2D} is the dipole-dipole interaction to M_2

$$M_{2D} = 3\, I(I+1)/N\, \Sigma_{(i\neq)}\, D_{ij}^2 \ . \qquad (9)$$

The full second moment M_2 in Eq.(1) is equal

$$M_2 = M_{2D} + M_{2CS} \ , \qquad (10)$$

where

$$M_{2CS} = \omega_0^2/N\, \Sigma_{(i)}\, (\sigma^i_{ZZ})^2 \qquad (11)$$

is the nuclear-electron (chemical shift) contribution to M_2.

Inserting Eq.(8) in Eq.(1) and using Eq.(10) we have

$$V(t,\tau) = [\, G_0(t)G_0(\tau) + (1/M_2)\, dG_0(t)/dt\, dG_0(\tau)/d\tau \,] -$$

$$-\, (M_{2CS}/M_2^2)\, dG_0(t)/dt\, dG_0(\tau)/d\tau + \dots \ . \qquad (12)$$

As was shown in [4]

$$G_0(t)G_0(\tau) + (1/M_2)\, dG_0(t)/dt\, dG_0(\tau)/d\tau \approx G_0(t-\tau)\ . \qquad (13)$$

Using Eq.(13) we obtain from Eq.(12) the following expression for the solid-echo signal

$$V(t,\tau) = G_0(t-\tau) - (M_{2CS}/M_2^2)\, dG_0(t)/dt\, dG_0(\tau)/d\tau + \dots\ . \qquad (14)$$

In Eq.(14) the first term describes the solid-echo signal. The second term in Eq.(14) leads to the attenuation and the shift of the echo signal amplitude. We may estimate these shift and attenuation assuming the Gaussian shape of the FID

$$G_0(t) = \exp(-M_2t^2/2)\ . \qquad (15)$$

The Gaussian shape of the FID is a good approximation for the short time t.
Inserting Eq.(15) into Eq.(14) gives

$$V(t,\tau) = 1 - (M_2/2)\,(t-\tau)^2 - M_{2CS}\, t\tau + \dots\ . \qquad (16)$$

From Eq.(16) it follows that maximum of the solid-echo signal has been observed at

$$t_e = \tau\,(1 - M_{2CS}/M_2)\ . \qquad (17)$$

Eq.(17) shows that he formation of a well-defined echo requires $M_{2D} >> M_{2CS}$.
The amplitude of echo signal is

$$V(t_e,\tau) = 1 - M_{2CS}\,(1 + M_{2D}/M_2)\,\tau^2\ . \qquad (18)$$

Eq.(17) and Eq.(18) show that the chemical shift interactions induce indeed the attenuation and shift of the solid-echo signal.
If $M_{2D} >> M_{2CS}$ we may write Eq.(18) in the form

$$V(t_e,\tau) = 1 - 2M_{2CS}\tau^2 + \dots \approx \exp(-2M_{2CS}\tau^2)\ . \qquad (19)$$

From Eq.(19) we see that it should be possible to estimate M_{2CS} from the attenuation of the maximum solid-echo amplitude at $\tau \to 0$.
The dipole-dipole interaction H_D is the „homogeneous" Hamiltonian, but the chemical shifts Hamiltonian H_{CS} is „non-homogeneous" one [5]. So this Hamiltonian can lead to the

formation of the Hahn's echo signal – signal which appears after the two-pulse sequence $90^0{}_Y - \tau - 180^0{}_X - t$. For the Hahn's pulse sequence the Hamiltonian H in Eq.(2) has the form

$$H = \exp(-i\pi I_X)\, H_{int} \exp(i\pi I_X) \ . \qquad (20)$$

Using Eqs.(4)÷(7) and Eq.(20) we obtain from Eq.(2)

$$a_{11} = M_{2D} - M_{2CS} \ . \qquad (21)$$

Inserting Eq.(20) in Eq.(1) and using Eq.(10) and Eq.(13) we obtain

$$V(t,\tau) = G_0(t-\tau) - (2M_{2D}/M_2^2)\, dG_0(t)/dt\, dG_0(\tau)/d\tau + \ldots \ . \qquad (22)$$

Assuming again the Gaussian shape of the FID (Eq.(15)) we obtain from Eq.(22) that the Hahn's echo signals has its maximum at

$$t_e = \tau\,(1 - 2M_{2D}/M_2) \ . \qquad (23)$$

From Eq.(23) it follows that the formation of the Hahn's echo signal in homonuclear spin system requires $M_{2CS} >> M_{2D}$.

The amplitude of the echo signal is ($M_{2CS}>>M_{2D}$)

$$V(t_e,\tau) = 1 - 2M_{2D}\,(1 - M_{2D}/M_2) + \ldots \approx \exp(-2M_{2D}\tau^2) \ . \qquad (24)$$

From Eq.(24) we see that the attenuation of the Hahn's echo signal is defined by the dipole-dipole interactions. It should be possible so to determined M_{2D} from the attenuation of the Hahn's echo signal.

References

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